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## ENCAPSULATING AGENTS WITH CONTROLLED WATER REPELLENCY

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This invention relates to a method for encapsulating substances, such as flavoring oils and perfumes, and to the products thus obtained. More particularly, this invention relates to novel water-repellant encapsulating agents and to the water-repellant encapsulated products derived therefrom. It is the object of this invention to provide encapsulating agents which, unlike those of the prior art, are characterized by their unusual water-repellancy. A further object involves the use of these encapsulating agents in the preparation of solid compositions containing entrapped therein volatile, relatively water-insoluble, flavors, perfumes and other substances, wherein it is desirable that said compositions display a controlled degree of water-repellancy and water resistance.

The use of volatile flavoring oils and perfumes in such applications as foods and cosmetics is often greatly hampered by the rapid evaporation and loss of the volatile component. Thus, although the practitioner may prepare a food, cosmetic or other product which initially contains the appropriate degree of flavor or fragrance, the ultimate consumer often finds that there has been a considerable reduction in these properties. This loss will, of course, detract from the desirability as well as from the utility of the products concerned. While we have spoken here mainly of foods and cosmetics, the same problem holds true wherever it is necessary to entrap volatile substances, whether in connection, for example, with pharmaceuticals, pesticides, detergents or the like.

Various techniques have been proposed to overcome this problem. These procedures generally involve the preparation of solid compositions containing the volatile ingredient entrapped therein. Such compositions may be prepared, for example, by mixing the volatile oil with a suitable absorbent base. In another method, the volatile materials are dispersed with solutions of various protective colloids, in which form they are dried and ground.

Of late, the technique of spray drying has found wide acceptance as a means for preparing solid particles containing entrapped flavors, perfumes or other water-insoluble, volatile substances. In this technique, the volatile oils are first emulsified in an aqueous solution of a water-dispersible protective colloid such as gelatine, gum arabic, starch or dextrine. This emulsion is then sprayed into a column of heated air or gases, which evaporates the water. It is believed that the dry particles resulting from that process comprise a shell or capsule of the dried colloid, in which the oil is imbedded, or encapsulated, in the form of minute droplets. The oil may also possibly be absorbed in the colloid base. Instead of spray drying, other drying means have also been proposed, such as spreading the emulsion on belts and passing through drying tunnels, or drying on heated drums, and the like. These procedures permit volatile, water-immiscible oils or other substances to be put into a solid, highly water-dispersible form which easily lends itself to blending with a wide variety of other ingredients, while also offering protection against the evaporation of the volatile component from the dry particles. Among the possible applications for such encapsulated oil particles, one may list their use in foods, cosmetics, spices, pharmaceuticals, soaps, deter-

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gents, bleaches, pesticides and cleansers. Other suitable uses will be apparent to those in the art, since any active ingredient may be thus entrapped.

In these applications, the encapsulated particles have heretofore always been characterized by their extreme water solubility. This property has been considered essential in order to make possible the ready release of the flavor, perfume or the like, at such time as the encapsulated particles are moistened or dispersed in water.

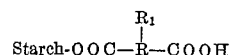
There are some applications, however, where it is desirable or necessary to effect a more gradual or controlled release of the entrapped substance. Thus, for instance, in making encapsulated insecticides, soil-sterilizing chemicals or weed killers, where it may be desired to obtain release of the active chemicals over a prolonged period, the use of the ordinary water-soluble encapsulating agents would give poor results. The soluble encapsulating materials would dissolve entirely too rapidly, releasing their contents prematurely. Other situations where rapid solution of the encapsulated particle would be a distinct disadvantage will be apparent to the practitioner. Although a more water repellent form of encapsulated particle would be of great value in such circumstances, the preparation of such products has not been possible, by the use of heretofore known encapsulating agents.

It is important to note that if one were to depart from the present practice of using highly water soluble encapsulating agents, such as dextrans or natural gums, and go to the other extreme of obtaining a completely water insoluble encapsulated granule, this would hardly solve the problem, since the flavors or perfumes would then be permanently imprisoned and rendered quite ineffective. Also if one were to begin by employing a completely water insoluble agent, it is not seen how such agent could be dissolved in water to serve as the medium in which to emulsify the oil or other volatile substance, prior to drying to achieve encapsulation or entrapment.

We have now solved this problem by employing as the encapsulating agent a substance which, while originally dispersible in water, forms a film upon drying which is water-repellent. The encapsulated particle produced by the use of such an encapsulating agent can be called neither completely water-soluble nor water-insoluble. Rather, it is one which permits a slow, gradual release of the entrapped material, in the presence of moisture. We refer to the encapsulated particles of our invention as having a controlled degree of water-repellency.

By the process of our invention, using the special encapsulating agents of the type herein described, we are able to obtain encapsulated particles which require a much longer exposure to moisture, as compared to particles prepared with the heretofore used water-dispersible colloids, in order to release the entrapped flavors, perfumes, or other substances. This property of controlled water-repellency causes the particles of our invention to be ideal for the encapsulation of slow-acting pesticides, sterilizing agents, certain pharmaceuticals, flavors and perfumes, where a slower, more gradual release of the entrapped substance is desirable.

As the encapsulating agent which may be dispersed in water but which forms a relatively water-repellent dried film, we prefer a particular type of starch derivative. This is the reaction product of a compound containing a polyvalent metallic ion, with an ungelatinized starch acid-ester of a substituted dicarboxylic acid. Such starch acid-esters may be represented diagrammatically by the following formula:



where R is a radical selected from the class consisting of dimethylene and trimethylene radicals, and R<sub>1</sub> is a hydro-